MOLECULAR ASSOCIATION IN ACETONE AND METHYL-ETHYL KETONE*

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(*Received for publication, July 2, 1940*)

Plate XXII

ABSTRACT. The Raman spectrum of acetone is studied in different solvents: water, methyl alcohol, phenol and acetic acid at different concentrations. In all these cases, the C=O line of acetone is found to shift towards smaller frequencies, while its C–C line and some of the deformation frequencies are found shifting towards higher frequencies. In acetic acid, a new line at 1760 cm.$^{-1}$ is obtained. These results are explained on the basis of the formation of hydrates in water, and complexes between the acetone molecules and those of the solvent in which it is dissolved. While these solvents produce such conspicuous changes, non-polar solvents like benzene and carbon-tetrachloride and normal polar solvents like ether and chloroform do not produce any effect on the Raman spectrum of acetone. Thus acetone seems to associate only with molecules having an acceptor atom. Similar results obtained with methyl ethyl ketone are similarly explained.

MOLECULAR ASSOCIATION IN ACETONE AND METHYL-ETHYL KETONE

INTRODUCTION

The application of Raman effect to the problem of molecular association has been the subject of recent investigations by the author. Ramakrishna Rao[1] first applied it to the study of water and interpreted the structural variations of the Raman water band with temperature as being due to the changes in the relative intensities of its three maxima which are themselves due to the presence of polymers of the type $(H_2O)_3$, $(H_2O)_2$ and H_2O. An application of the same method to heavy water by Ramakrishna Rao and the author [2] revealed similar intensity variations in its Raman band with temperature and these variations were again explained as due to the change in the equilibrium between three types of polymers in heavy water also $(D_2O)_3$, $(D_2O)_2$ and D_2O. Extending the work to other associated liquids, the author studied the Raman spectra of acetic,[3] formic and benzoic acids [4] in their solutions in water and at different temperatures. The intensity maximum of the band due to the carbonyl frequency in all the acids studied was found to be shifting towards higher frequencies on dilution in aqueous solutions and with increased tempera-

* Part of the thesis approved for the D.Sc. degree of the Madras University.

** Communicated by the Indian Physical Society.

tures. These results were explained on the assumption that the molecules of the fatty acids are initially associated and that they break up at higher temperatures into their lower polymers as in the case of water and heavy water and also that they depolymerise in the presence of a highly associated solvent like water.

To study the behaviour of acetic acid in other solvents also, the Raman spectra of this substance in mixtures with both polar and non-polar liquids were taken.[5] Therein it was found that in non-polar solvents like benzene and carbon tetrachloride, acid molecules are not affected, the Raman spectrum of the mixture being just a superposition of the spectra of the individual components. But in other polar solvents, nitrobenzene, ether, acetone and methyl-ethyl ketone, the C=O line consisted of two definite lines, one at 1670 as in the pure acid and another at 1760, which was attributed to the externally unattached C=O in the complex formed between the acid and the solvent. Further evidence for the formation of the complexes was got by a study of the acetone lines which are themselves affected in the presence of acetic acid. A detailed study of the behaviour of acetone and methyl-ethyl ketone, not only in solutions in acetic acid but in a number of other solvents, gives an insight into the capacity of these ketones to associate with other dissimilar molecules.

EXPERIMENTAL

The experimental arrangement used was the usual Wood's tube with a iodine trough. $NaNO_2$ solution was used to filter off 4046-line of the mercury arc and the other lines of lower wavelengths. The liquids were rendered free from water and vacuum-distilled.

RAMAN SPECTRUM OF ACETONE

The Raman spectrum of acetone was investigated by a large number of workers, prominent among them being Dadieu and Kohlrausch[6], Whitelaw[7], Ganesan and Venkateswaran[8], Dillon Dicknisen[9], Sirkar[10], Edsall[11] and Engler[12]. Bates, Anderson and Halford[13] studied Dentero-acetone. As acetone gives sharp lines, there are no discrepancies with regard to its Raman frequencies. Kohlrausch gives the Raman frequencies for the liquid as the mean of the frequencies observed by a number of workers. The intensities of the lines are mentioned in brackets opposite each frequency. 376(2), 490(1), 526(3), 788(10), 901(0), 925(1b), 1060(3), 1193(3), 1223(5), 1340(0), 1430(5b), 1712(5) 2925(10), 2969(2), 3003(2).

Edsall worked with aqueous solutions of acetone and found no shifts in the frequencies. Whiting and Martin[14] working with acetone and carbon disulphide mixture detected no effect.

Gordy,[15] working in the infra-red region, reported a shift of C=O absorption in acetone towards longer frequencies in heavy water and chloroform solutions.

He could not study the effect of water upon the C=O frequency due to the superposition of the absorption band of water in the same region. In a recent publication[16], he found a new absorption frequency at 4μ in mixtures of acetone and chloroform and attributed it to the frequency due to the hydrogen bond −H...O−, between the O in C=O and H in C−H in chloroform. This he claimed as the first discovery of the direct spectrum of the hydrogen bond, all other evidences being indirect, based upon the changes in the frequencies of the bands closest to that of hydrogen.

RAMAN SPECTRUM OF METHYL-ETHYL KETONE

The Raman spectrum of this liquid was studied by Dadieu Kohlrausch[6], Whitelaw,[7] Ganesan and Venkateswaran[8] and Kohlraunch and Koppl[17]. Due to discrepancies in the measurements by various workers, the author again measured the frequencies, and the results obtained by the different authors are given below.

TABLE I

Ganesan and Venkateswaran	Whitelaw	Kohlrausch and Koppl	Author
—	310(1)	253(1)	—
408 2)	406(0)	408(3)	408(4)
560(2)	593(2)	592(3)	560(4)
766(4)	764(6)	763(7)	765(10)
964(1)	955(0)	947(1b)	950(1)
..	—	1001(1b)	1000(1)
1003(1)	1085(4)	1088(3)	1090(1)
1176(0)	1165(0)	1165(½)	1198(4)
1207(0)	1213(0)	—	1220(1)
...	—	1247(½)	1250(1)
1375(1)	1356(1)	--	1357(3)
1431(3)	1436(2)	1412(3b)	1420(5)
—	—	1450(3b)	1450(5)
1729(2)	1734(3)	1711 ± 10(3b)	1712(7)
2876(2)	—	—	2915(3)
2936(4)	2928(6)	2917(10b)	2925(86)
3651(1)	2948(3)	2980(6b)	2975(2)

EFFECT OF DIFFERENT SOLVENTS ON THE RAMAN SPECTRUM OF ACETONE

Different solvents were chosen for studying their effect on the molecules of acetone. They are (*i*) non-polar—benzene and carbon-tetrachloride, (*ii*) polar and normal chloroform, ether, (*iii*) polar and abnormal—water, methyl alcohol, phenol and acetic acid. The results obtained in all these cases are given below.

(*i*) *Non-Polar* : Benzene and carbon-tetrachloride has no effect on the Raman spectrum of acetone as was the case on acetic acid. This is in accordance with Whiting and Martin's observation that carbon-disulphide also had no effect on acetone.

(*ii*) *Polar and Normal* : Among the normal polar solvents studied, ether and chloroform differ in the fact that ether does not have a hydrogen atom to link up to the O in C=O in acetone. Both the liquids, acetone and ether, have donor atoms O. Hence there was naturally no effect of either of the molecules on the other. In the case of chloroform, it has got a hydrogen atom linked up to the carbon and recent solubility and infra-red data point out the possibility of the H in chloroform having acceptor properties. In fact, Gordy reported the absorption due to the hydrogen band between O in C=O in acetone and the H in chloroform. But even prolonged exposures with mixtures of acetone and chloroform did not give any trace of a line or band in the region 4μ ($\Delta\nu$=2500) as indicated by Gordy or in the region of the familiar OH band ($\Delta\nu$=3200—3600). The spectrum of the mixture was just the superposition of the spectra of the individual components as in the previous case. There was no shift of any of the acetone lines or of the chloroform lines as reported by Gordy in the infra-red region.

(*iii*) *Polar and Abnormal* : This class of liquids brought about conspicuous changes in the Raman spectra of acetone. The results with each one of the liquids are given *seriatum* :

(1) *Water* : Edsall reported no shifts of the C=O line in solutions of acetone in water. But the author observed shifts not only of the C=O line but of a number of other lines of acetone. Raman spectra of solutions containing 90%, 75%, 50% and 25% by volume of acetone in water were compared with that for the pure liquid and the following changes were observed in dilute solutions :—

(*a*) The line 1712 attributed to the C=O frequency, definitely shifted gradualiy to smaller frequencies with increasing concentration of water.

(*b*) The line 788 attributed to the C—C oscillation shifts gradually to longer frequencies.

(*c*) The lines 530, 1069, 1223, 1340 shift to longer frequencies with increasing dilution.

(*d*) The line 370 becomes very weak at higher dilutions.

788 1712

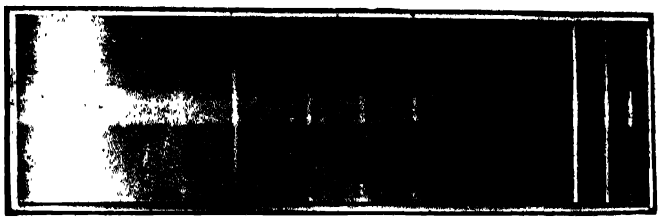


Fig. 1 (a) Acetone pure

75% + Water 25%

789 1712

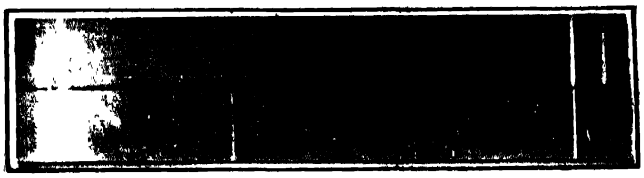


Fig. 1 (b) Acetone 25 + Water 75

1712

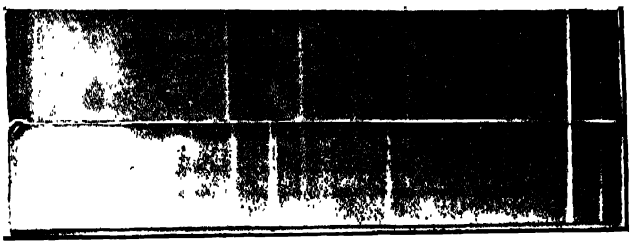


Fig. 1 (c) Pure Acetone

Acetone 34% + Phenol 68%

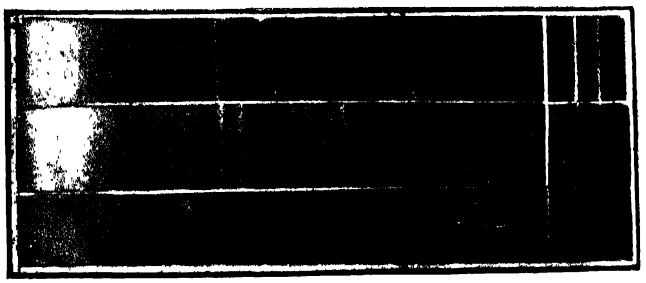


Fig. 1 (d) Acetone Pure

Acetone 50 + Acetic Acid 50

Acetic Acid Pure

ure

30

765 1712

Fig. 1. Acetone in different Mixtures.
Fig. 2. Methyl Ethyl Ketone + Water

Figure 1 (*a*) gives the Raman spectra of pure acetone as compared with that of a 75% solution in water. 1 (*b*) compares pure acetone with a 25% solution.

The following table gives the approximate frequencies of the C–C and the C=O lines at the different concentrations :–

TABLE II

C–C and C=O frequencies of Acetone in Aqueous Solutions

Percentage of acetone	C–C	C–O
Pure	788	1712
90%	793	1706
75%	796	1704
50%	799	1702
25%	800	1696

Measurements are from microphotometric curves under high magnification.

(2) *Methyl Alcohol* : Methyl alcohol did not produce as pronounced an effect as in the case of water. But a slight shift in the C=O line at 1712 towards shorter frequencies is perceptible. In the microphotometric curve of the Raman spectrum of a 50:50 mixture, the C=O line shows a structure with two peaks. The 1223-line shows a distinct shift at higher dilutions.

(3) *Phenol* : Phenol produces very conspicuous shifts on the lines of acetone. Four different concentrations were studied with increasing proportions of phenol by weight, (*viz.*) 53%, 40%, 34% and 13% of acetone in the mixtures. The percentages are by weight. In the solutions, the C=O band at 1712 again definitely shifts to shorter frequencies and the C–C line at 788 shifts to longer frequencies. Observations of the shifts of the C–C line are difficult due to the presence of the 812-line of phenol close to it and to the high-frequency side of it, but a closer scrutiny reveals the shift in this line. Among the other lines, the shift in the 530-line cannot be observed on account of the superposition of a line due to phenol, and the 1223-line gets more diffuse and shows a large shift towards higher frequencies. This is due to the superposition of the 3059-line of phenol excited by the 4046-mercury-line, which is transmitted feebly through the sodium-nitrite filter. The 1340-line seems to be suppressed in solutions. Figure 1 (*c*) compares the Raman spectrum of pure acetone with that of a mixture containing 34% acetone and 68% of phenol.

(4) *Acetic Acid* : Acetic acid again produces pronounced effects on the Raman spectrum of acetone. The effect of acetone on the Raman pectrum of acetic acid has been discussed in a previous publication.[5] The effect

of acetic acid on acetone is given here. Three concentrations 75%, 50%, and 25% by volume of acetone in the solutions were studied. The effect on the C=O line of acetone cannot be studied with precision due to the superposition of the shifted C=O line of acetic acid on it, but a perusal of the spectra and their microphotometric traces points out to the probability of the C=O line having shifted towards low frequencies as in the other cases described above. But the shifting of the C—C line at 788 towards higher frequencies is quite clear and the effect can be traced to acetone alone, as there is no acetic-acid line in that region. Figure 1 (*d*) gives the Raman spectra of acetone, acetic acid and a 50:50 mixture of acetone and acetic acid. The new line at 1760 makes its appearance in all the three concentrations. It is marked by an arrow in figure 1 (*d*) It is very clear in the 50:50 mixture by volume. The lines 530, 1069, 1223, and 1340 have shifted to longer frequencies. The effect can be taken to be that of acetone as in the 50% mixture, the time of exposure being reduced in order not to excite the feeble lines of acetic acid in that region.

SUMMARY OF THE RESULTS

(1) In solutions of acetone in non-polar solvents like benzene and carbon-tetrachloride, the Raman lines are unaffected, the spectrum of the mixture being an exact superposition of the spectra of the individual components.

(2) Similar is the case in solutions of acetone in normal polar solvents—chloroform and ether. The acetone lines are unaffected by the presence of the solvent.

(3) Water, methyl alcohol, phenol and acetic acid produce distinct changes in the Raman spectrum of acetone, the main alterations being a shift of the 1712-line towards shorter frequencies, and a corresponding shift of the 788-line towards higher frequencies. The lines 530, 1069, 1223, and 1340 shift towards higher frequencies in mixtures of acetone with water and acetic acid, while in methyl alcohol, the 1223-line shifts towards higher frequencies. In phenol it is not possible to study these lines on account of their very feeble excitation and due to their superposition on the phenol lines. The shift is progressive in all these solutions, higher dilutions producing greater shifts.

EFFECT OF SOLVENTS ON METHYL-ETHYL KETONE

Similar results were obtained with methyl-ethyl ketone. Non-polar solvents like benzene and carbon-tetrachloride and normal polar solvents like ether and chloroform do not produce any effect on the ketone. The effect of water and acetic acid is exactly similar to that on acetone. Fig. 2 gives the effect produced by water in a 30% solution of the ketone (by volume). The C=O line at 1712 is again shifted to lower frequencies. The C—C line at 765 is shifted to higher

frequencies. The 590-line is also slightly shifted to higher frequencies and the effect of the other lines could not be studied due to their feebleness.

The effect of acetic acid on the ketone is again similar to that on acetone The low-frequency shift of the 1712-line cannot be studied distinctly on account of the superposition of the shifted C=O of the acetic acid. The effect on the C—C 765-line, (*viz.*) its high-frequency shift, is detectable. The new line at 1760 can be seen in a mixture of the ketone in the acid (50 : 50 by volume).

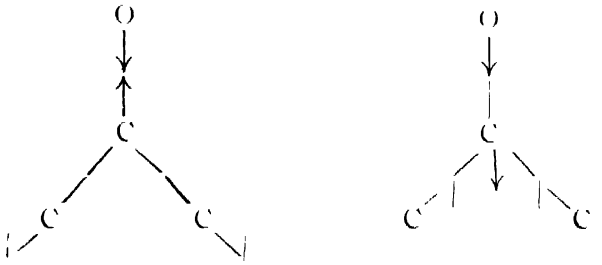
DISCUSSION OF THE RESULTS

The results outlined above point out to a definite change in the molecular structures of acetone in abnormal polar solvents like water, methyl alcohol, phenol, acetic acid, while no such change is noticed in non-polar solvents like benzene and carbon-tetrachloride and in polar normal solvents like ether and chloroform. That the non-polar solvents do not have any effect on the solutes (the words solvent and solute are used merely to indicate the two components of the mixture with no special significance such as that the solvent is the larger component by weight or by volume) is well-known and is explained by the fact that they cannot have any dipole interaction producing molecular association or dissociation on the solute for the simple reason that they do not possess any dipoles. In the case of polar normal liquids, the behaviour of ether is again plain as molecular association can take place only when a donor and an acceptor atoms are present in the mixture. Both ether and acetone have donor atoms and hence there cannot be a hydrogen bonding between them. Recent infra-red data by Gordy and his co-workers and the solubility data of Gladstone and others led to the supposition that chloroform can form hydrogen bonds through its hydrogen acting as an acceptor. As has been stated already, Gordy claimed to have recorded the hydrogen bond between acetone and chloroform But the author's work on Raman spectra does not lend suport to the conclusion. Even supposing that the band excited by the hydrogen bond is infra-red active and Raman inactive, there must be a pronounced effect on the C=O oscillation in acetone. In fact Gordy reports a shift in the C=O towards higher frequencies. But no such shift is observed by the author in the Raman spectrum of the mixture of acetone and chloroform.

On the other hand, abnormal liquids like water, phenol, acetic acid, and methyl alcohol produce marked changes on the Raman spectrum of acetone. The shift of the C=O line towards shorter frequencies is very significant. In previous publications,[3,4] it was argued that association must bring about a decrease in the frequency of the C–O bond. The effect of the external attachment like the hydrogen bond was pointed out to be towards a diminution of the C=O binding. The fact that water of crystallisation diminishes the frequency of the NO_3-ion in a number of nitrates was also pointed out in support of the contention. In the present work, there is direct evidence of such

a diminution of the C=O frequency by an external attachment. The strong donor O of the C=O in acetone seems to form a hydrogen bond with the H in OH of the solvent, and hence the diminution of the C=O frequency. But Gordy reports a shift of the C=O to higher frequencies in mixtures of acetone in heavy water. The author's results in water mixtures are again in contrast to this observation.

Another very remarkable change is noticeable in solutions of acetone in abnormal solvents in the C—C line. This line at 788 shifts to higher frequencies in solutions in water, phenol, methyl alcohol and acetic acid. This change is also attributable to the formation of the complex. Probably the effect of the external hydrogen bonding upon this frequency is to increase it, as compared to the decrease in the C=O frequency. The molecular oscillations in these cases can be represented as follows :



$\omega_1 = 1712$ $\omega_2 = 788$

For the same external force field, if ω_1 diminishes, ω_2 may increase on account of the differing nature of the two oscillations. Kohlrausch and Koppl attribute the values 370, 530, and 1069 to deformation frequencies ω_5, ω_3 and ω_4 respectively. As it is not proposed to get into the discussion about the assignment of the frequencies in this paper, it is merely stated that the shifts in frequencies 530, 1069, 1223, and 1340 are all due to the formation of the complex itself, the deformation frequencies as well as the higher overtones also being affected in addition to the symmetrical and antisymmetrical oscillations.

A perusal of the microphotometric curves of the Raman spectra of acetone at different dilutions and a comparision of the same with the curves for the C=O frequencies in acetic acid and in formic acid at different dilutions shows that in all these cases the shift of the intensity maximum is progressive. In the case of acetic and formic acids, the shift of the C=O is towards longer frequencies and, in the case of acetone, it is towards shorter frequencies in aqueous solutions. The two progressive shifts in opposite directions suggest two opposing effects on the molecular structure. While in the one case, acetic and formic acids, it is towards a strengthening of the C=O bond probably caused by the breaking up of the higher polymers into lower ones, in the case

of acetone, the shift indicates a weakening of the bond, caused by an external attachment and hence by the association of acetone with water. There is another argument. Supposing that the high-frequency shift of the C=O in fatty acids in aqueous solutions is due to hydrate formation, then the low-frequency shift in acetone solutions must be due to the breaking up of the complexes. Acetone is a normal liquid and no complexes exist in the pure state. Hence, the low-frequency shift in acetone must be due to the formation of a hydrate and correspondingly the high-frequency shift in the fatty acids to the breaking up of the associated complexes.

The progressive nature of the shift can be easily understood, as with increasing dilution, the percentage of complexes in the mixture increases and hence, the intensity maximum of the band shifts progressively towards the direction of the frequency of the C=O in the complex.

Another distinguishing feature in aqueous solutions of both the fatty acids and of acetone is that, though it is the intensity maximum that shifts, the total width of the band remains more or less the same In the case of acetic acid, the band is broad even in the pure state, and it remains so at almost all the dilutions studied, except at every high dilutions when it shows a tendency to sharpen. In the case of acetone, the C=O oscillation is revealed by a slightly diffuse line and it remains so at all dilutions.

Thus the main part of the evidence for the formation of association complexes is :

(1) The shift towards low frequencies of the C=O line in acetone.

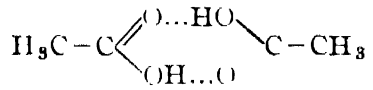
(2) The corresponding shift towards higher frequencies of the C—C line.

(3) Shifts of the other lines, 530, 1069, 1223 and 1340, towards higher frequencies.

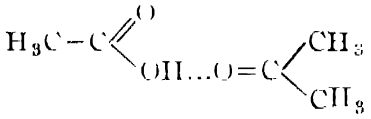
In cases like acetic acid where the shift of the C=O line cannot be clearly detected, the other two evidences help to postulate the possibility of the complex-formation. The shifting of the C—C line and the other deformation frequencies in acetone-acetic acid mixtures, in addition to the evidence of the C=O line itself which can be seen shifted to lower frequencies in plates which are not sufficiently exposed to record the acetic acid lines clearly, points out to the formation of an associational complex with the acid as with the other solvents—water, methyl-alcohol, and phenol. Thus the C=O line at 1760 is attributed to the externally unattached C=O of the complex. Detailed reasons for doing so are explained *elsewhere*.* [5]

The next problem is whether acetone breaks up the association of the solvent and attaches itself to the monomers liberated or whether it attaches itself to the higher polymers themselves. In acetic acid, this question can be partially answered. In the dimer or in any higher complex, both the donor and

acceptor atoms are closed up within a ring structure with hydrogen bonds interposed as follows :



For the acetone to associate with the acid molecule, it must necessarily break up the polymer in order to liberate the H. Thus association may take place between acetone and the monomer of the acid liberated, as follows :



This breaking up of the higher polymers into lower ones has also been inferred from the fact that the C=O line of acetic acid shifts towards higher frequencies in acetone solutions as in the case of dilution in water and at higher temperatures. In other solvents it is not easy to detect the same effect, since they do not form closed-ring structures even on association, both the donor and the acceptor atoms being at either end of the polymer and free to associate A study of the water band in acetone solutions by Sambasiva Rao[18] revealed a sharpening of this band indicating that the higher polymers $(H_2O)_3$ break up into lower ones $(H_2O)_2$ and H_2O. But the water band is a composite one involving also that excited by the water that has hydrated with the acetone molecules.

EFFECT ON METHYL-ETHYL KETONE

The effect of normal and abnormal solvents on methyl-ethyl ketone is exactly similar to that on acetone. Dilution brings about a shift of the C=O line towards higher frequencies. Solution in acetic acid also gives rise to similar changes. Hence the ketone seems to form complexes with acetic acid as in the case of acetone.

This work was done in 1939 in the Physics Laboratories of the Andhra University, Waltair, under the direction of Dr. I Ramkrishna Rao, to whom the author desires to express his gratitude.

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* Paper No. 34, this Journal